PQI-3401 – Engenharia de Reações Químicas II

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Kinetics of Heterogeneous Catalytic Reactions

CATALYST DEACTIVATION

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Catalyst Deactivation

C_t reduces with time of use of the catalyst on process

Activity of the catalyst (definition)

$$a(t) = \begin{pmatrix} \text{activity of} \\ \text{the catalyst} \end{pmatrix} = \frac{\text{reaction rate at time t (used catalyst)}}{\text{reaction rate at time t = 0 (fresh catalyst)}} = \frac{(-r_A)'\big|_t}{(-r_A)'\big|_{t=0}}$$

For a fresh catalyst, $a(t=0)=1$

Rate of deactivation r_d

$$r_d = -\frac{da}{dt} = k_d(T)\,f(a)\,h(C_A, C_B, \ldots)$$

$$f(a) = a^0 \quad \text{(zero order decay of activity)}$$

$$f(a) = a^1 \quad \text{(1st - order decay of activity)}$$

$$f(a) = a^2 \quad \text{(2nd - order decay of activity)}$$

etc.

Catalyst Deactivation

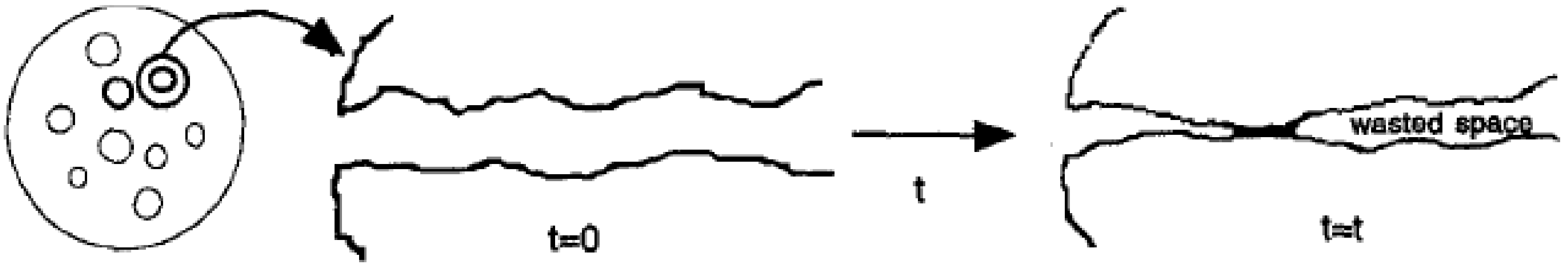
Types of deactivation

(1)Deactivation by Sintering or Aging

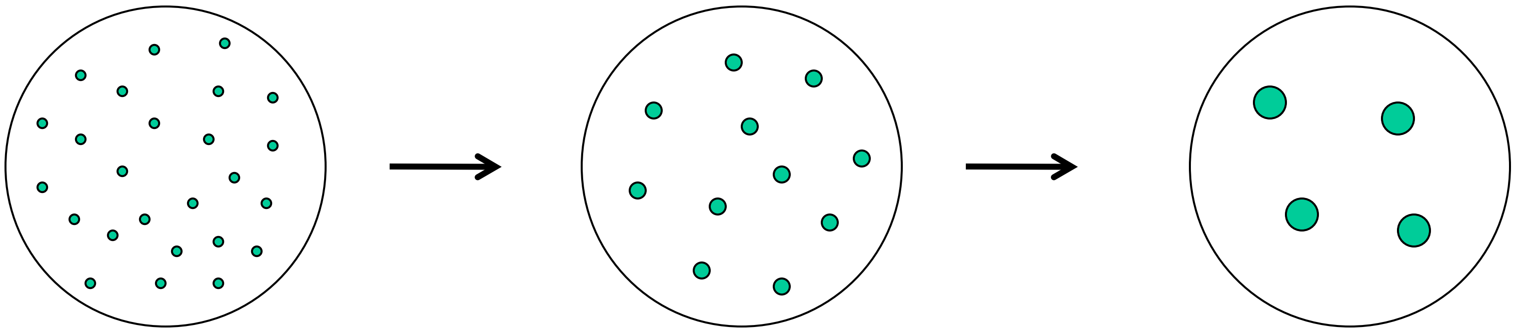
(2)Deactivation by Coking or Fouling

(3)Deactivation by Poisoning

Catalyst Deactivation by Sintering / Aging / Structural changes



Pore closure (structural degradation)



Sintering (metallic supported catalyst)

Catalyst Deactivation by Sintering

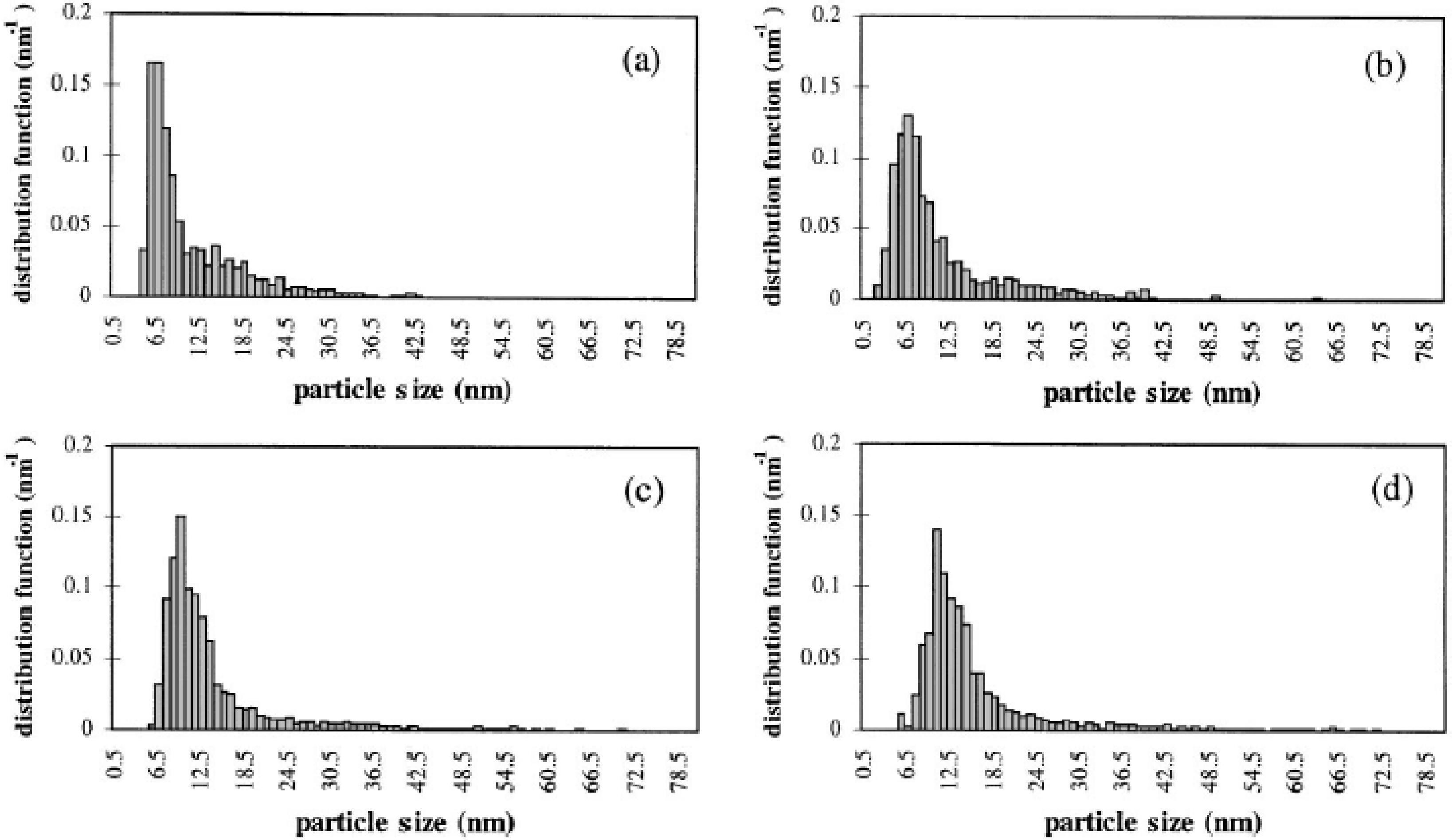


Fig. 4. Particle size distributions determined by TEM for catalyst COPR-900 as a function of sintering time. (a) as reduced; (b) 5 h; (c) 15 h; (d) 30 h.

Teixeira & Giudici, *Chem. Eng. Sci. 54 (1999) 3609-3618*

Catalyst Deactivation by Sintering

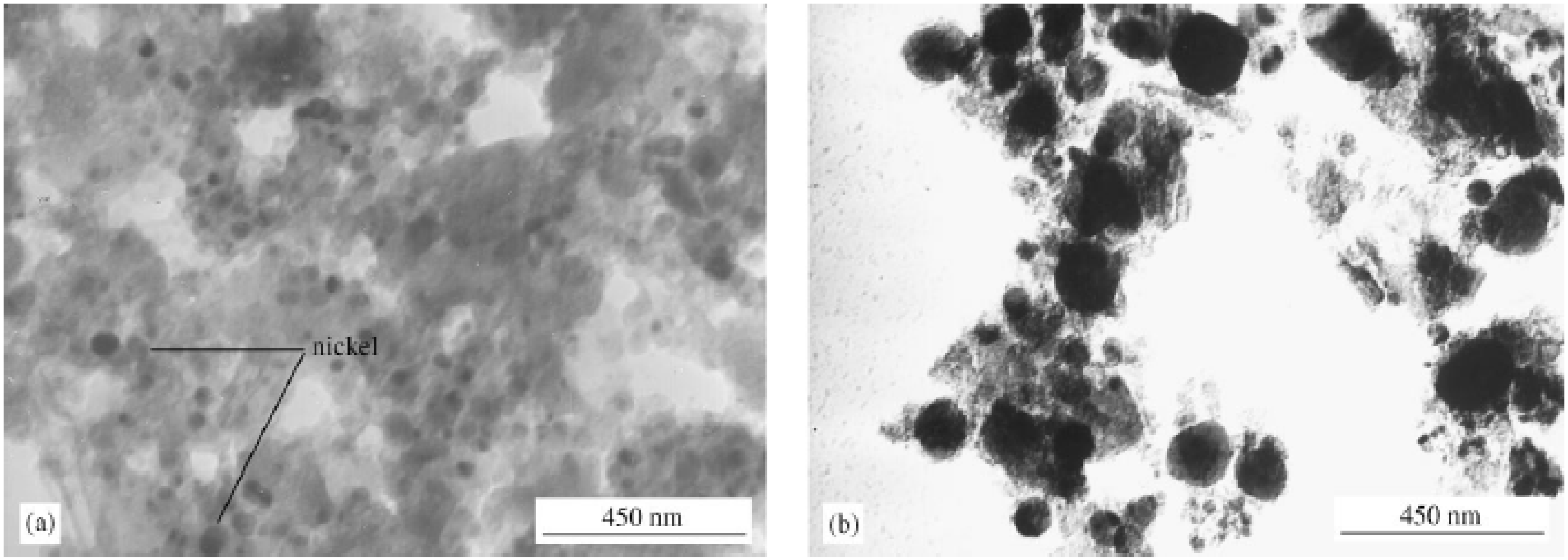


Fig. 5. TEM micrographs of catalyst COPR-450 after 5 h sintering (a), and after 30 h sintering (b), under steam reforming of CH_4 at 800°C.

Teixeira & Giudici, *Chem. Eng. Sci. 54 (1999) 3609-3618*

Catalyst Deactivation by Sintering

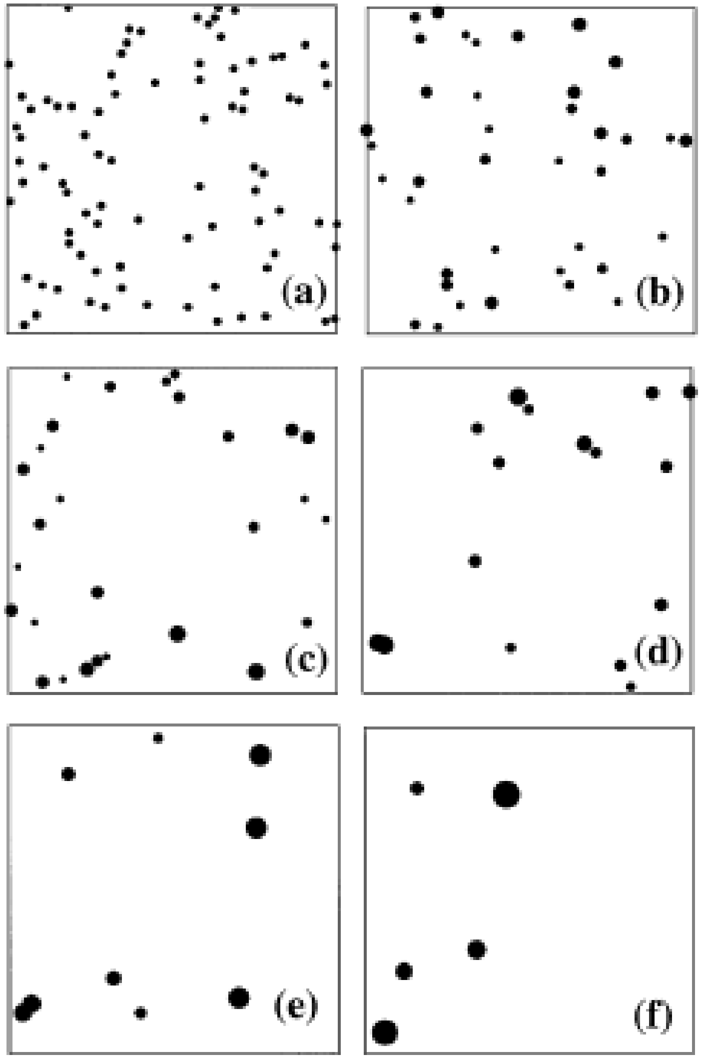
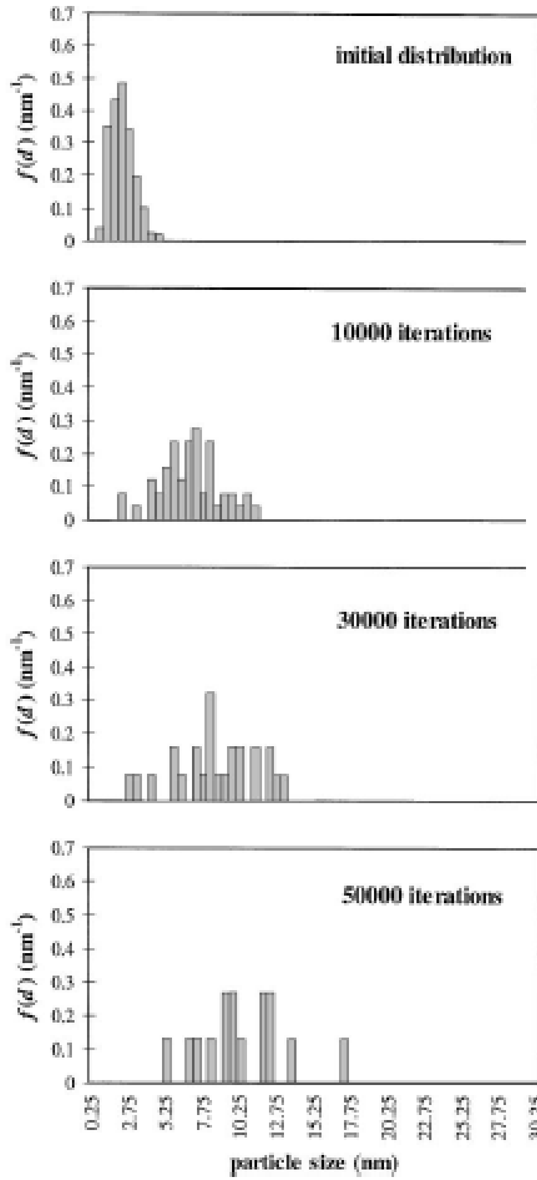


Fig. 5. Location of metal particles during sintering: (a) uniform initial PSD with 5 nm crystallites; (b) 5000 iterations; (c) 10 000 iterations; (d) 20000 iterations; (e) 30000 iterations; and (f) 90000 iterations.



6. Evolution of PSD as predicted by the model. Initial PSD with mean 2 nm and standard deviation 1 nm.

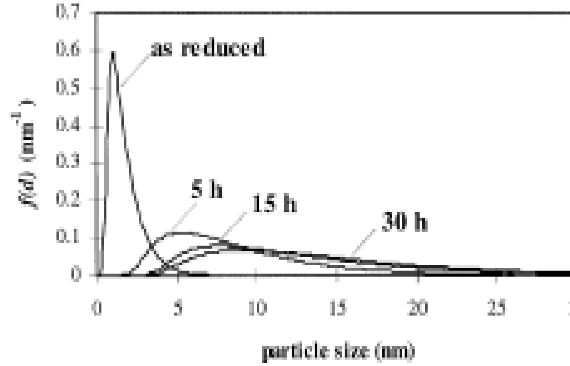
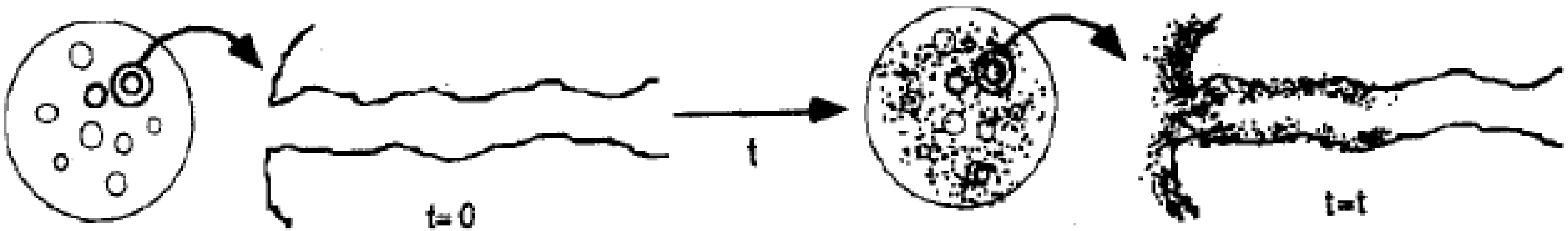


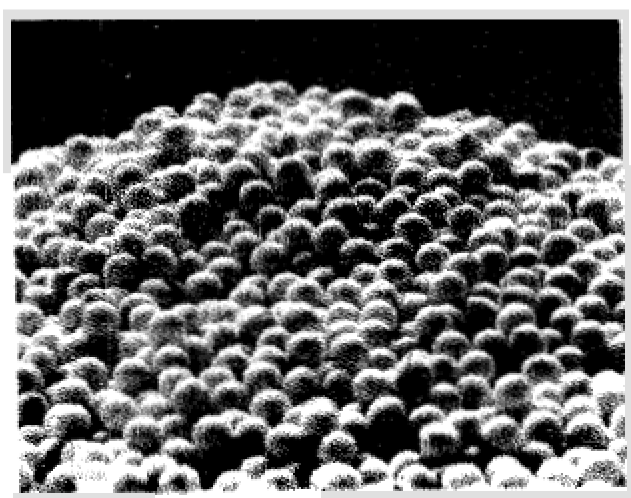
Fig. 7. Evolution of PSD for a coprecipitated Ni/Al_2O_3 catalyst sintered under steam reforming reaction at 800°C. Initial PSD with mean 1.78 nm and standard deviation 1.03 nm (Teixeira & Giudici, 1999).

Teixeira & Giudici,
Chem. Eng. Sci. 56 (2001) 789-798

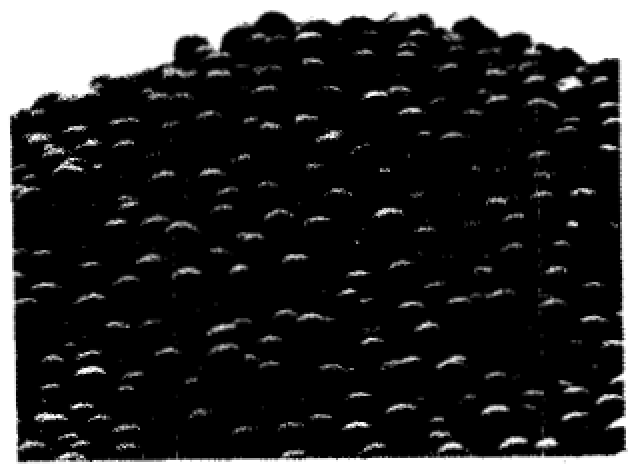
Catalyst Deactivation by
Coking / Fouling / formation of coke



Coke = carbonaceous material formed from decomposition of reactants and/or products



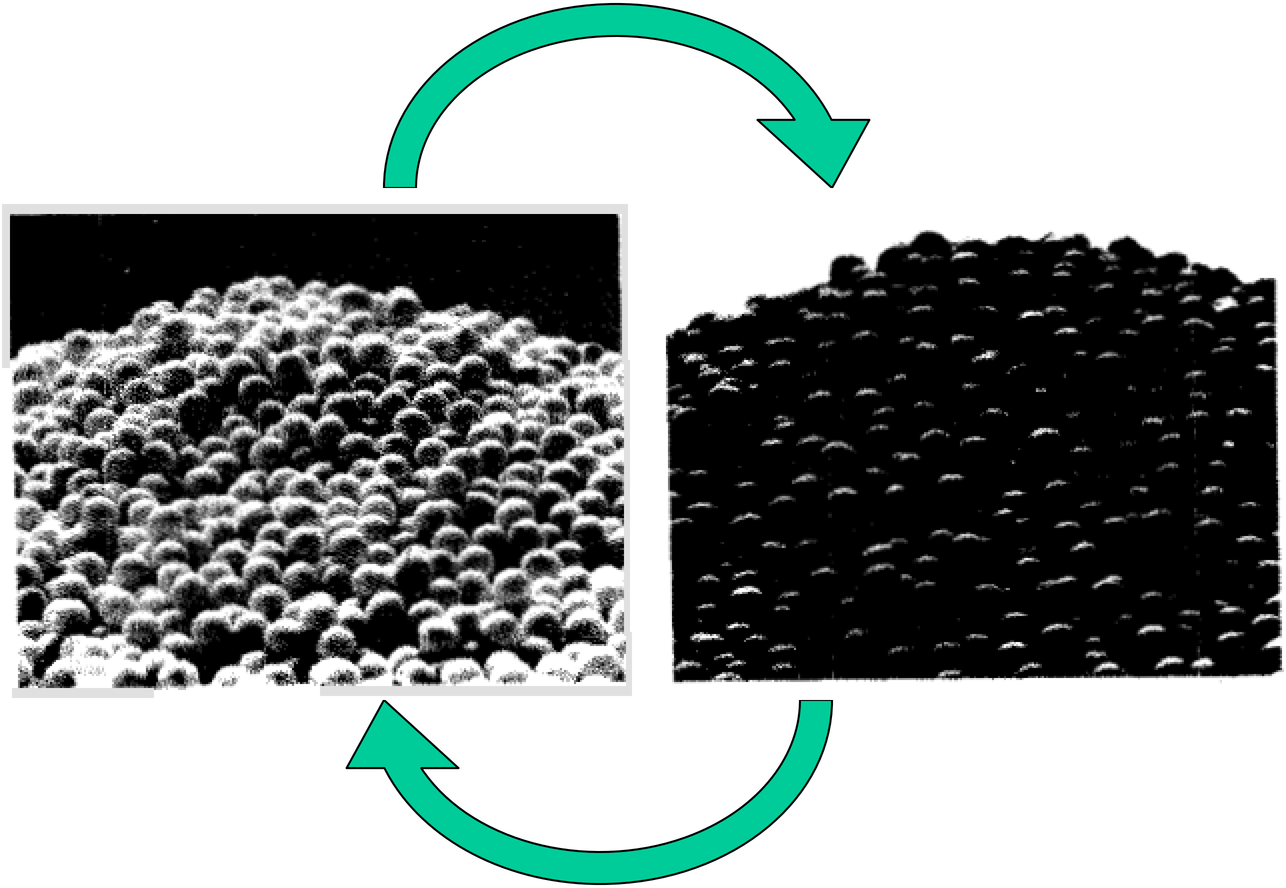
(a) Fresh catalyst



(b) Spent catalyst

Catalyst Deactivation by Coking / Fouling

Coking (during catalyst use on process)



Regeneration by controlled burning (slowly, ~1-2% O_2)

Catalyst Deactivation by Coking / Fouling and Regeneration

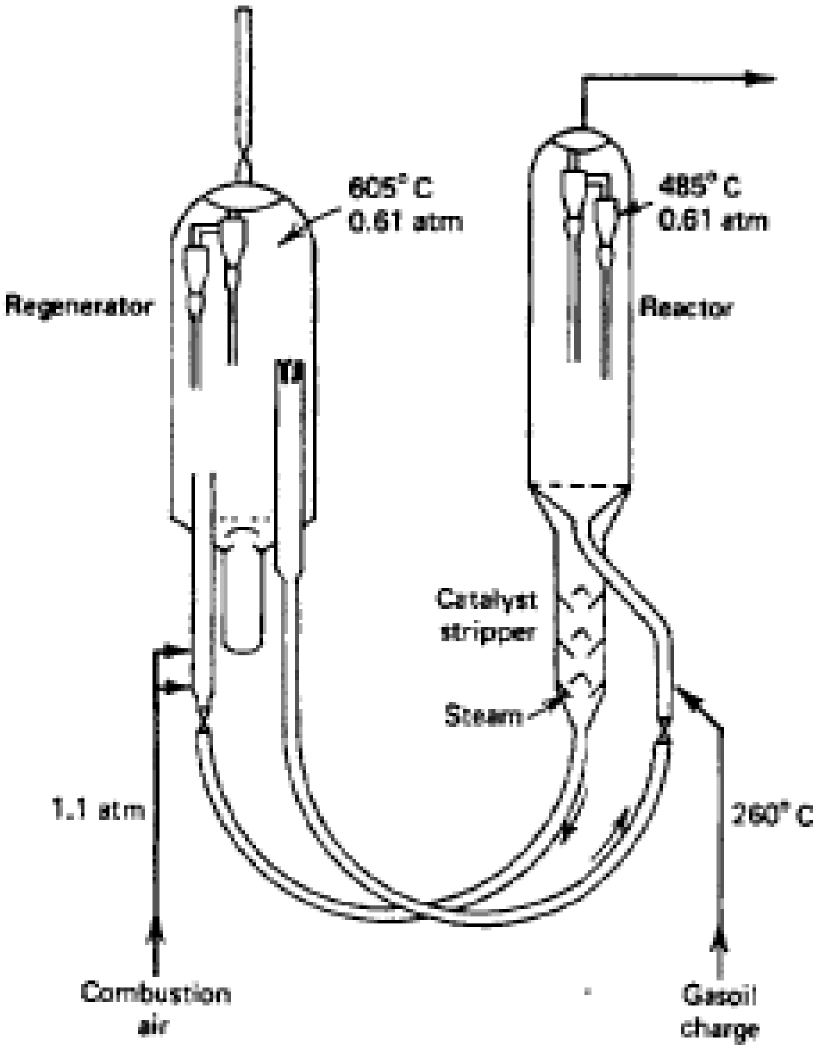


Figure 13.2-1 Reactor-regeneration system for catalytic cracking of gasoil (after Zenz and Othmer [10]).

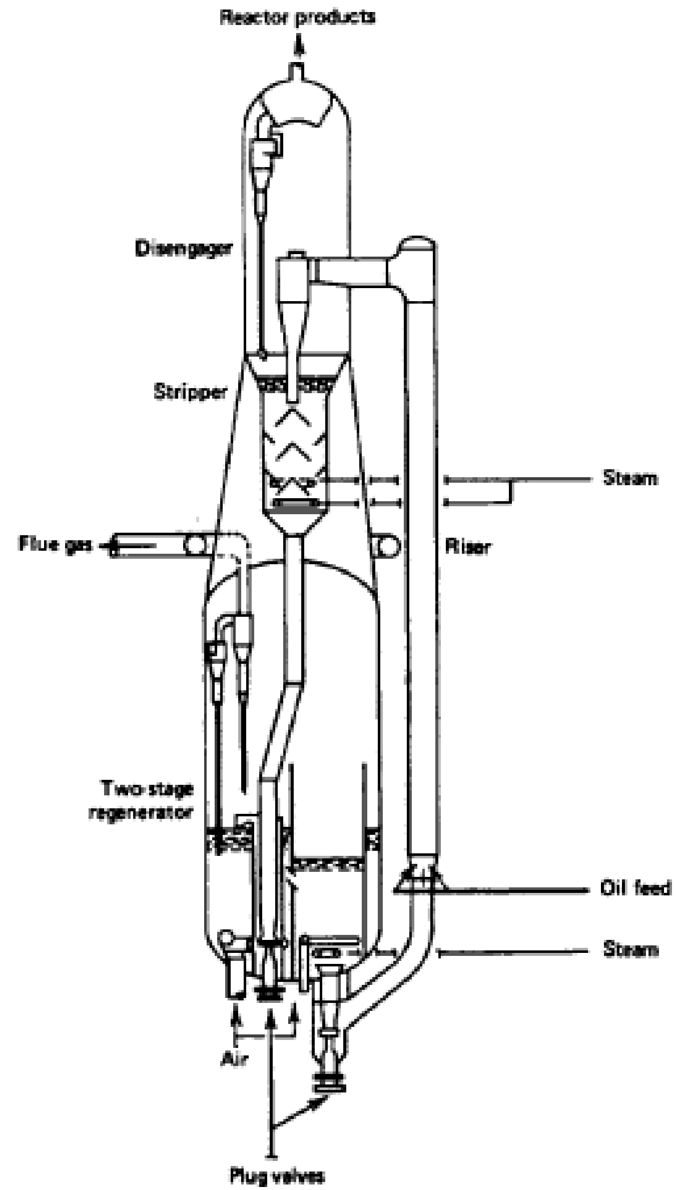
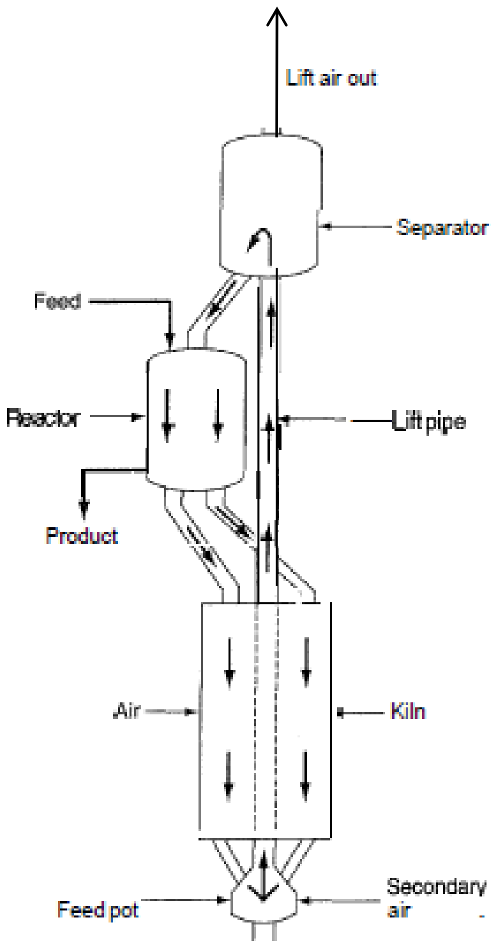


Figure 13.2-2 Kellogg orthoflow model F convertor with riser cracking and two-stage regeneration (from Murphy and Soudek [30]).

Catalyst Deactivation by Coking / Fouling and Regeneration



Arrows show catalyst circulation

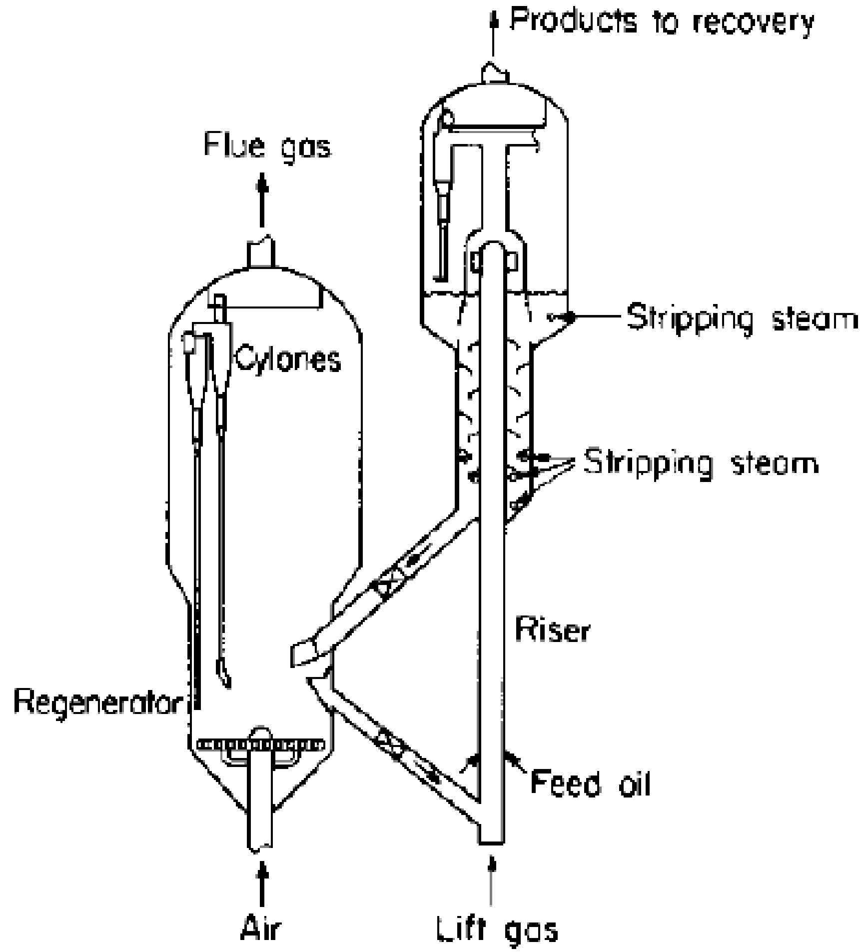


FIGURE 9.18 Modern FCC unit.

Catalyst Deactivation by Poisoning

Poison = impurities present in the feeding stream that are chemiosorbed irreversibly to the active sites (thus reducing the number of sites)

e.g., sulfur compounds (H_2S, mercaptans),
arsenium compounds, etc.

$$A \rightleftarrows B$$

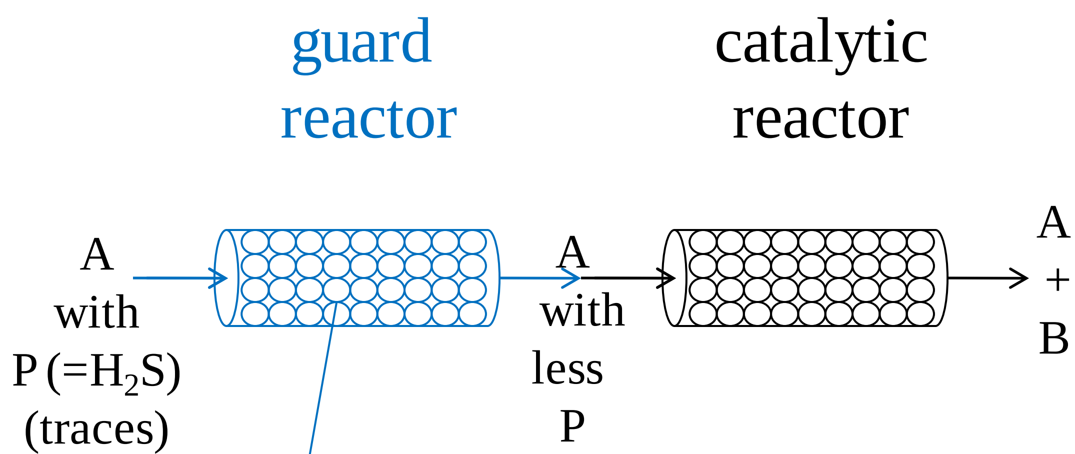
Mechanism

$$A + S \underset{}{\overset{1}{\rightleftarrows}} AS$$

$$AS \underset{}{\overset{2}{\rightleftarrows}} BS$$

$$BS \underset{}{\overset{3}{\rightleftarrows}} B + S$$

$$\boxed{P + S \xrightarrow{4} PS}$$



$$\boxed{H_2S_{(g)} + ZnO_{(s)} \rightarrow H_2O_{(g)} + ZnS_{(s)}}$$

Deactivation kinetics

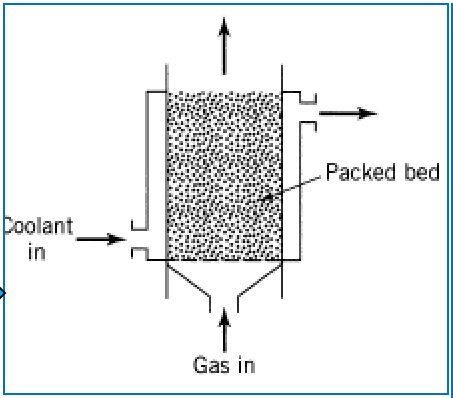
- Zero-order $$-\frac{da}{dt} = k_d \qquad a(t) = 1 - k_d t$$
- 1st-order $$-\frac{da}{dt} = k_d a \qquad a(t) = \exp(-k_d t)$$
- 2nd-order $$-\frac{da}{dt} = k_d a^2 \qquad a(t) = \frac{1}{1 + k_d t}$$

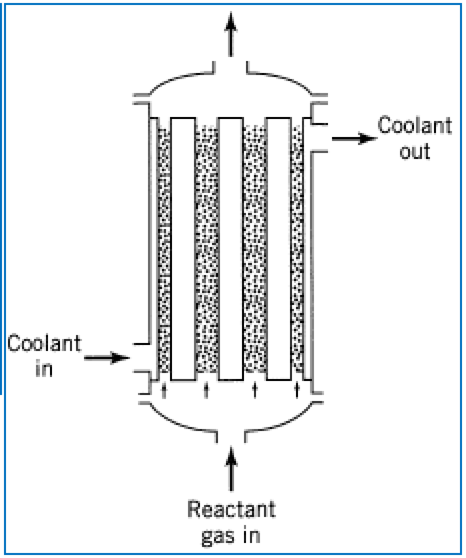
Deactivation kinetics and reactor type

DEACTIVATION RATE		REACTOR TYPE
• Slow (years/months)	→	• Packed-bed reactor (+ *T(t) trajectory*)
• Moderate (weeks, days)	→	• Moving-bed reactor
• Fast (hours, minutes)	→	• Fluidized bed (bubbling regime)
• Extremely fast (seconds)	→	• Straight-through transport reactor (pneumatic transport, riser, downer)

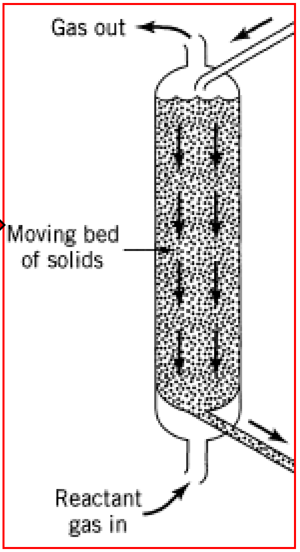
Reactor types

- Packed-bed reactor (+T(t) trajectory)

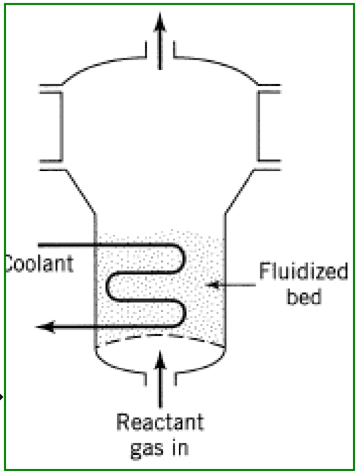




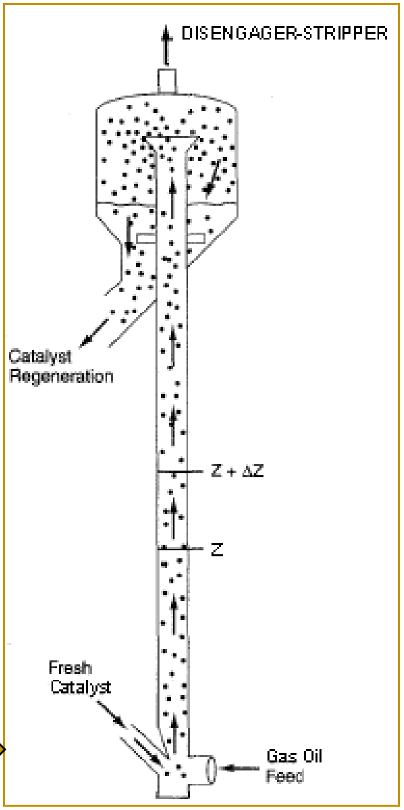
- Moving-bed reactor



- Fluidized bed (bubbling regime)



- Straight-through transport reactor (pneumatic conveying, riser, downer)



Temperature-time trajectory for packed-bed reactor

Temperature-time trajectory

Change T(t) to keep X_A=constant and $(-r_A)'$=constant

$$\underbrace{(-r_A)'\Big|_{t=0,T=T_0}}_{k(T_0)C_A^m} = (-r_A)'\Big|_{t,T(t)} = \underbrace{a(t).(-r_A)'\Big|_{t=0,T(t)}}_{a(t)k(T)C_A^m}$$

T↔a

a(T) or T(a)

$$k(T_0) = a(t)k(T) = a(t)k(T_0)\exp\left(-\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right) \quad \Rightarrow \quad \boxed{\frac{1}{T}-\frac{1}{T_0} = \frac{R}{E_A}\ln(a)}$$

$$-\frac{da}{dt} = k_d(T)a^n = k_d(T_0)\exp\left(-\frac{E_d}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)a^n = k_d(T_0)\exp\left(-\frac{E_d}{E_A}\ln(a)\right)a^n$$

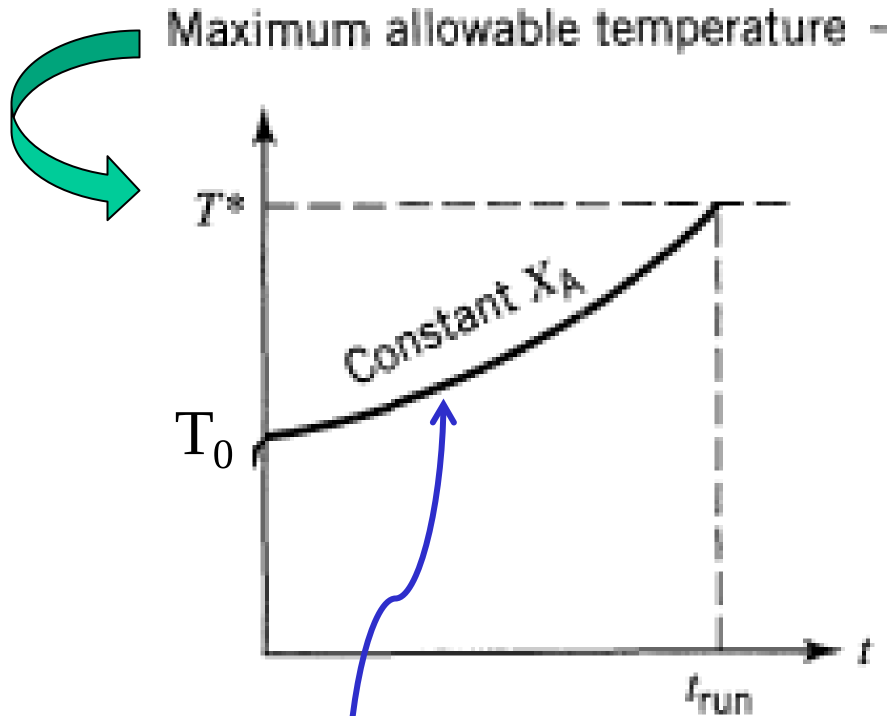
$$-\frac{da}{dt} = k_d(T_0)\, a^{\left(n-\frac{E_d}{E_A}\right)}$$

a↔t

a(t) or t(a)

$$\int_1^{a(t)} \frac{da}{a^{(n-E_d/E_A)}} = k_d(T_0)\int_0^t dt \quad \Rightarrow \quad \boxed{t = \frac{1-a^{(1-n+E_d/E_A)}}{k_d(T_0)[1-n+E_d/E_A]}}$$

Temperature-time trajectory



$$\boxed{\frac{1}{T}-\frac{1}{T_0}=\frac{R}{E_A}\ln(a)}$$

$$\boxed{t=\frac{1-a^{(1-n+E_d/E_A)}}{k_d(T_0)[1-n+E_d/E_A]}}$$

$$\Rightarrow \boxed{t=\frac{1-\exp\left(\frac{E_A-nE_A+E_d}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right)}{k_d(T_0)[1-n+E_d/E_A]}}$$

$t \leftrightarrow T$

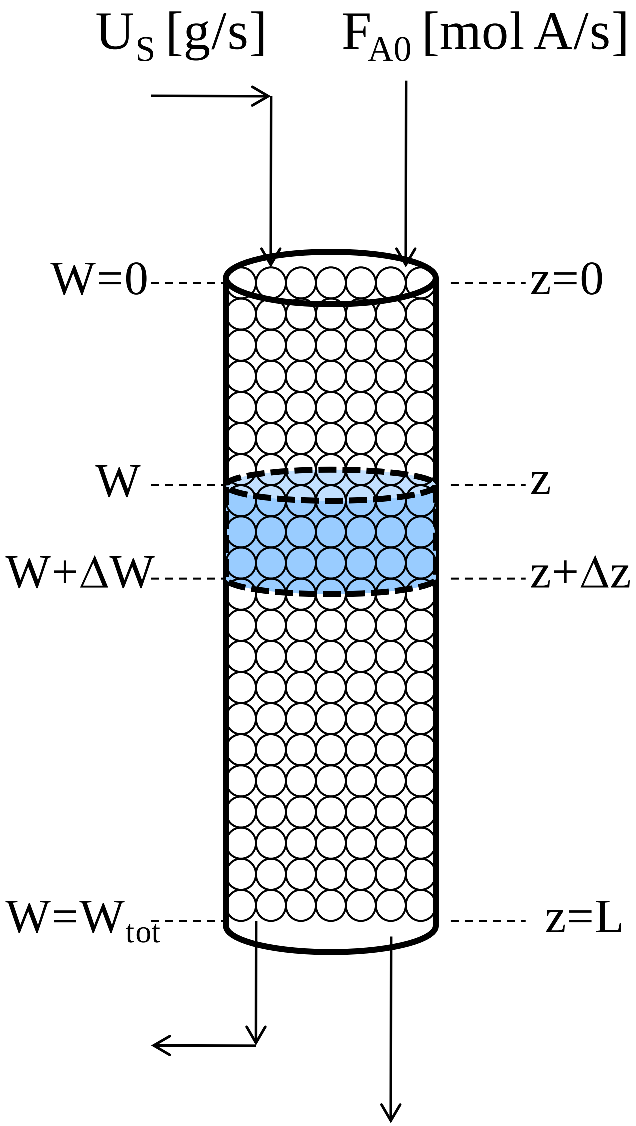
$T(t)$ or $t(T)$

Moving Bed Reactor

and

Straigth-through Transport Reactor

Moving-bed reactor



$$0 = \frac{d(C_A \Delta V)}{dt} = F_A\big|_z - F_A\big|_{z+\Delta z} + r_A \Delta V$$

$$W = \rho_b V = \rho_b A_c z$$

and

$$\Delta W = \rho_b \Delta V = \rho_b A_c \Delta z$$

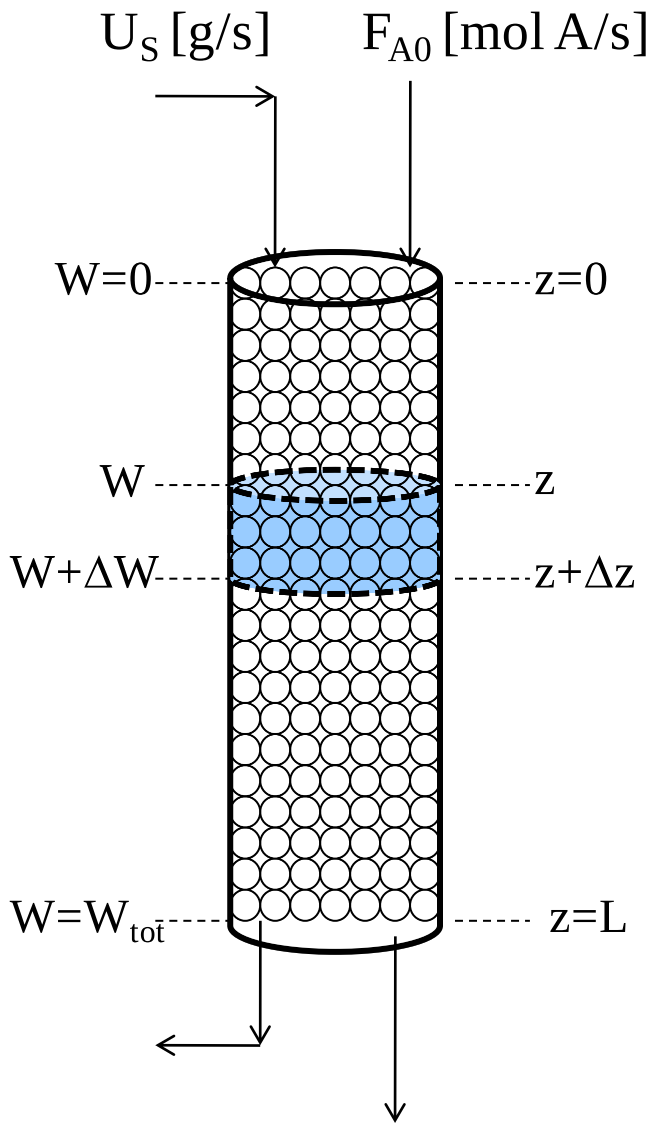
$$0 = \frac{d(C_A \Delta V)}{dt} = F_A\big|_W - F_A\big|_{W+\Delta W} + r_A' \Delta W$$

$$0 = F_{A0}\left(1 - X_A\big|_W\right) - F_{A0}\left(1 - X_A\big|_{W+\Delta W}\right) + r_A' \Delta W$$

$$F_{A0}\left(\frac{X_A\big|_{W+\Delta W} - X_A\big|_W}{\Delta W}\right) = -r_A'$$

$$\boxed{F_{A0}\frac{dX_A}{dW} = (-r_A')}$$

Moving-bed reactor

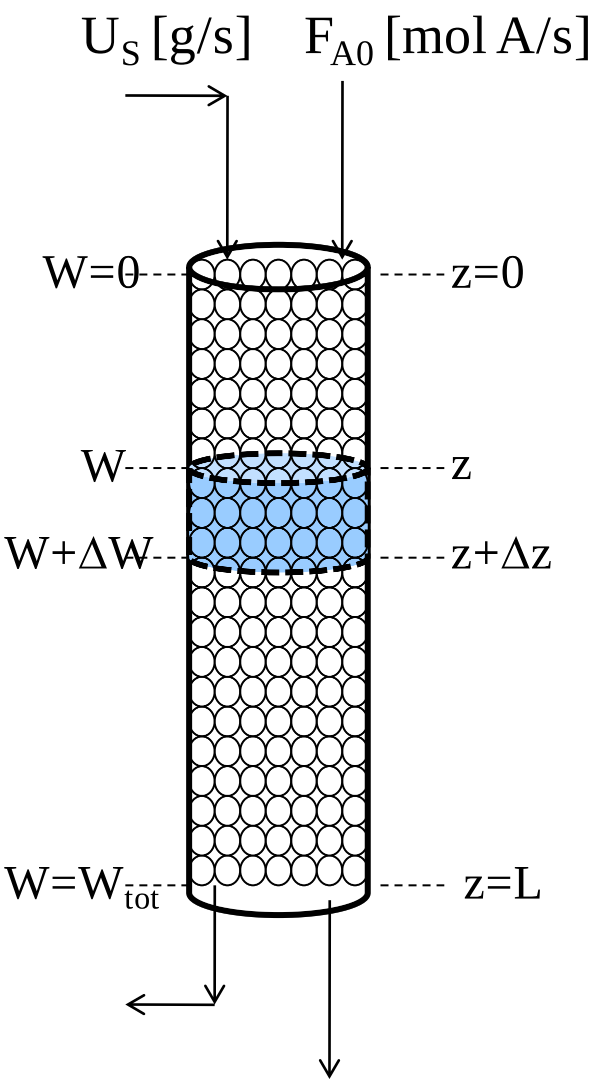


$$\left.\begin{aligned} F_{A0}\frac{dX_A}{dW} &= (-r_A^{'}) \\ (-r_A^{'}) &= a(t)(-r_A^{'})\Big|_{t=0} \end{aligned}\right\} \Rightarrow \boxed{F_{A0}\frac{dX_A}{dW} = a(t)(-r_A^{'})\Big|_{t=0}}$$

$$\left.\begin{aligned} -\frac{da}{dt} &= k_d a^n \\ dt &= \frac{dW}{U_S} \end{aligned}\right\} \Rightarrow \boxed{-\frac{da}{dW} = \frac{k_d}{U_S} a^n}$$

U_s = mass flow rate of catalyst [g/s]

Moving-bed reactor



Energy Balance (case 1: $T_s \neq T_g$)

$$\left.\begin{aligned} \sum_i F_i \tilde{c}_{pi} \frac{dT}{dW} &= +Ua_w\left(T_c - T\right) + ha_p\left(T_S - T\right) \\ U_S c_{pS} \frac{dT_S}{dW} &= (-r_A^{'})(-\Delta H_R) - ha_p\left(T_S - T\right) \end{aligned}\right\}$$

U = heat transfer coeff. between reactor (gas) and jacket

$$a_w = \left(\frac{\text{heat transfer area with external medium (jacket) at } T_c}{\text{weight of catalyst}}\right)$$

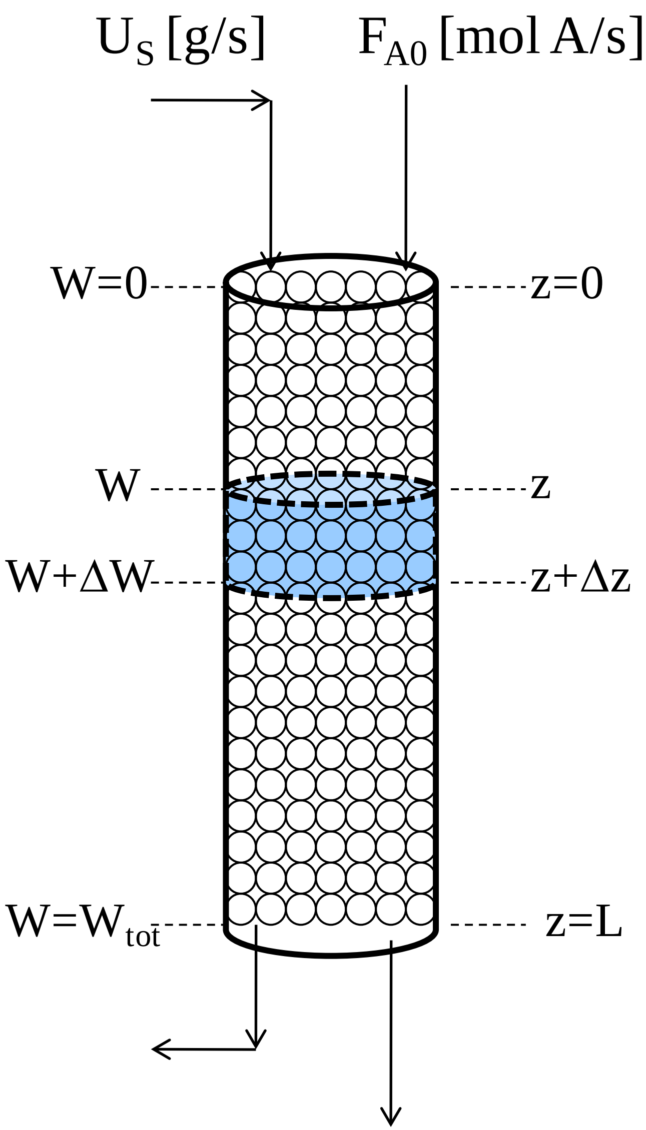
$$a_w = \frac{A}{W} = \frac{A}{\rho_b V} = \frac{\pi D_t L}{\rho_b \dfrac{\pi D_t^2}{4} L} \Rightarrow \boxed{a_w = \frac{4}{D_t \rho_b}}$$

h = heat transfer coef. between gas (T) and solid particles (T_s)

$$a_p = \left(\frac{\text{heat transfer area between gas - solid}}{\text{weight of catalyst}}\right)$$

$$a_p = \frac{A_p}{W} = \frac{A_p}{V_p \rho_b} = \frac{\pi d_p^2}{\dfrac{\pi d_p^3}{6} \rho_b} \Rightarrow \boxed{a_p = \frac{6}{d_p \rho_b}}$$

Moving-bed reactor



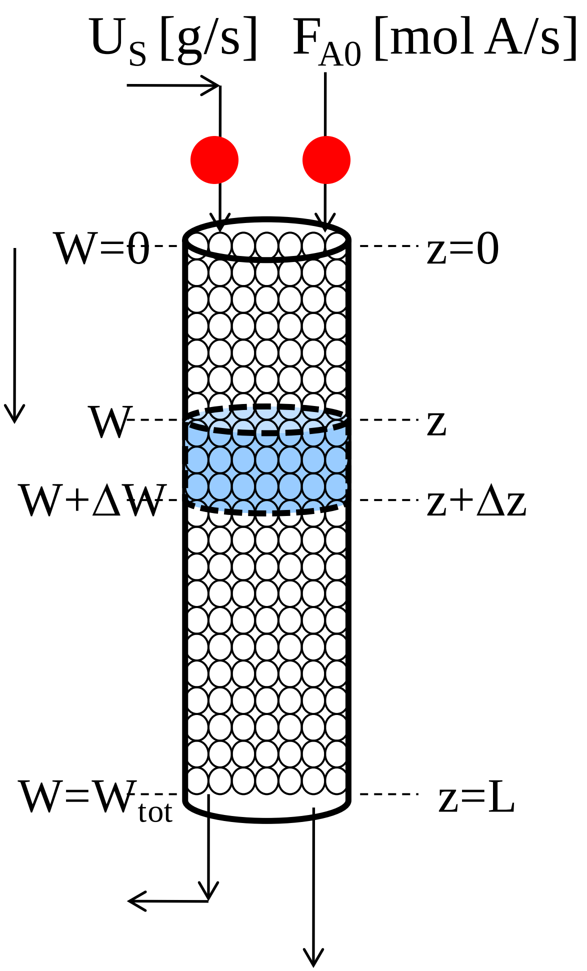
Energy Balance (case 1: $T_s \neq T_g$)

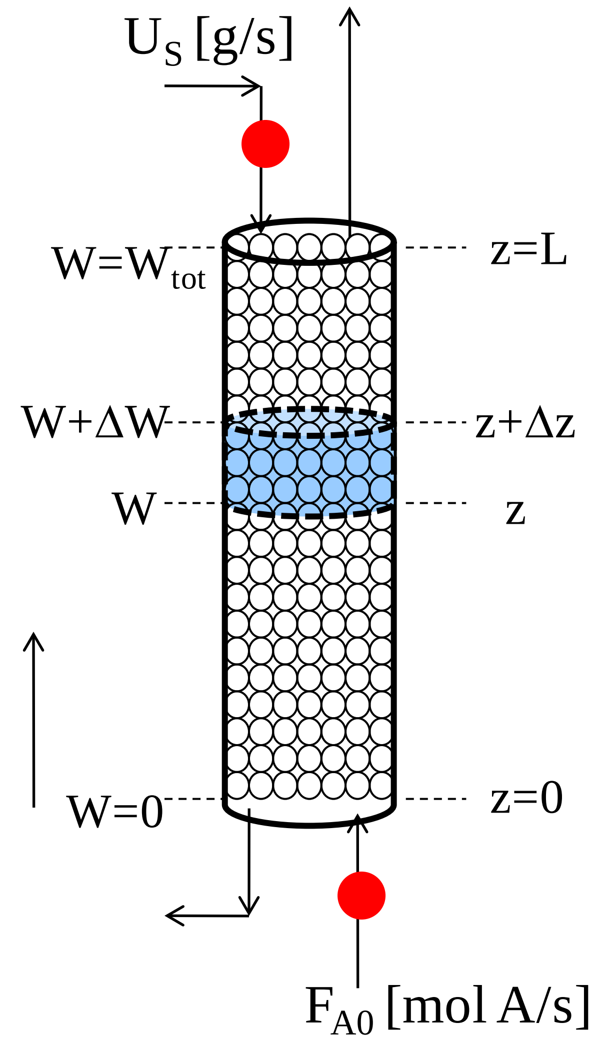
$$\left.\begin{aligned} \sum_i F_i \tilde{c}_{pi} \frac{dT}{dW} &= +Ua_w\left(T_c - T\right) + ha_p\left(T_S - T\right) \\ U_S c_{pS} \frac{dT_S}{dW} &= (-r_A')(-\Delta H_R) - ha_p\left(T_S - T\right) \end{aligned}\right\}$$

Energy Balance (case 2: $T_s = T_g = T$)

$$\left(U_S c_{pS} + \sum_i F_i \tilde{c}_{pi}\right)\frac{dT}{dW} = (-r_A')(-\Delta H_R) + Ua_w\left(T_c - T\right)$$

Moving-bed reactor (cocurrent and countercurrent)





Cocurrent boundary conditions

$$U_S > 0 \qquad a = 1 @ W = 0$$

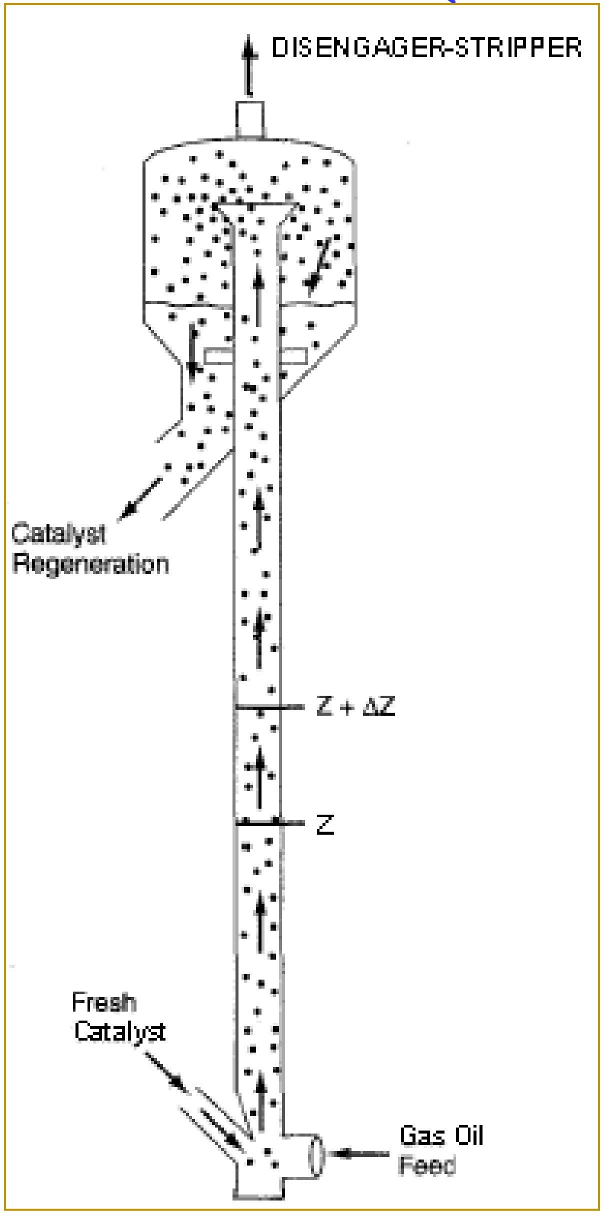
$$F_{A0} > 0 \qquad X_A = 0 @ W = 0$$

Countercurrent boundary conditions

$$U_S < 0 \qquad a = 1 @ W = W_{tot}$$

$$F_{A0} > 0 \qquad X_A = 0 @ W = 0$$

Straigth-through Transport Reactor (Riser, Downer)



Balance equations are
quite similar (actually the same ones)
as those of the Moving Bed Reactor
(but in this case there is only
the cocurrent configuration)

Catalyst Deactivation

Recommended Exercises
(Fogler Chapter 10)

P-10-18 (3ª. Ed.) = P-10-19(h) (4ª. Ed.)
P-10-15 (3ª. Ed.) = CD-P-10h (4ª. Ed.)
P-10-19 (3ª. Ed.) = P-10-20 (4ª. Ed.)
------- (3ª. Ed.) = P-10-21 (4ª. Ed.)
P-10-22 (3ª. Ed.) = P-10-23 (4ª. Ed.)